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EMULSIFIER FOR OIL-BASED DRILLING FLUIDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to emulsifier compositions and to the production of stable water-in-oil emulsions containing such emulsifier compositions. The emulsifiers of the present invention and the emulsions prepared therewith are especially suitable for use in the formation of water-in-oil drilling fluids, known as invert muds, of drilling wells to tap subterranean deposits of fluids, such as oil and/or gas.

2. Description of Related Art

It is often desired to prepare emulsions of water and oil. Emulsions of water in various oleaginous media wherein the oleaginous material is the continuous phase and water or aqueous material is the dispersed phase have been employed for numerous applications, such as oil well drilling muds, cutting oils, hydraulic fluids, lubricants, cosmetics, agricultural emulsions, and the like, where the lubricating, corrosion protection, or cosmetic characteristics of the oleaginous material is desired, and water or aqueous material serves to bring about fire resistance and the like. Such emulsions are commonly prepared prior to use so as to insure proper formulation, or they may be formed *in situ* where, for example, environmental moisture is emulsified, thereby reducing corrosion problems or preventing the water from being absorbed by the surroundings.

It is generally agreed among those skilled in the art that a rotary system is the most acceptable form of drilling a subterranean well. This system depends upon the rotation of a column of drill pipe to the bottom of which is attached a multi-pronged drilling bit. The bit cuts into the earth, causing the cuttings to accumulate as drilling continues. As a result, a

drilling fluid must be used to carry these cuttings to the surface for removal, thus allowing the bit to continue functioning, and the bottom hole to be kept clean and free of cuttings at all times. Drilling systems other than the rotary system are sometimes employed in drilling operations; nevertheless, these systems still require a drilling fluid to remove borehole cuttings, and to otherwise perform functions related to drilling fluids. In many instances, what is generally referred to as a "drilling fluid" actually may be utilized, with either no modification, or only minor modification, as a fluid for use in conjunction with completing or working over a subterranean well. In this regard, utilization of the phrase "drilling fluid" herein contemplates the utilization of such fluid in such completion and workover operations in subterranean wells, as well as in drilling operations.

Although aqueous-based drilling fluids which utilize clear water, brine, saturated brine, or sea water as the primary liquid base, may be found to be dominant within some facets of the drilling industry, there is a considerable need for drilling fluids wherein a hydrocarbon liquid forms the major liquid constituent, particularly in instances in which the drilling fluid is utilized in the higher temperature wells which are drilled to the more substantial depths.

Hydrocarbon-based drilling fluids normally are defined as invert emulsion, or water-in-oil emulsion, drilling fluids. These emulsions provide droplets of water that typically are dispersed in a continuous phase of oil. The oil comprises a hydrocarbon, such as mineral oil, diesel oil, crude oil, kerosene, a poly(alpha-olefin), or the like. The amount of oil used is normally within the range of about 60 to about 95 parts by volume, and preferably within the range of about 70 to about 90 parts by volume, on the basis of 100 parts equaling the liquid phase of the drilling fluid. At the higher level of the range, a drilling fluid with a comparatively lower viscosity will be produced, while drilling fluids having a lesser amount of oil will

produce a comparatively higher viscosity fluid. The concentration of the selected hydrocarbon depends upon the particular application for which the water-in-oil drilling fluid is to be used.

The dispersed liquid phase of the drilling fluid is normally referred to as the "water phase" and may consist of fresh water, salt water, sea water, or saturated brine. Normally, the presence of typical amounts of sodium chloride, calcium chloride, calcium carbonate, or calcium sulfate salts will have some, but no significant, effect on the stability of the emulsion produced. The water concentration should be in the range from between about 5 to about 40 parts by volume, and, preferably, will be within the range of about 10 to about 30 parts by volume, on the basis of 100 parts equaling the liquid phase of the drilling fluid composition. Again, the exact concentration depends upon the particular application for which the invert emulsion drilling fluid is to be used.

The liquid hydrocarbons normally serve as a continuous liquid vehicle to be converted into a drilling fluid having desirable properties for the desired applications by adding various materials to thicken the fluid so that it will support cuttings and provide a low fluid loss when the fluid is subjected to filtration against a permeable formation and in addition to increase the density of the fluid. As is known, oil-based drilling fluids are used for well-drilling associated with high temperature, high pressure and/or other difficult formations. In environmentally sensitive areas, synthetic or mineral base oils may be used. In such use, it is desirable to employ an oil base fluid having low filtration. It is also advantageous to use an oily fluid to minimize corrosion and to provide low fluid loss characteristics over lengthy time periods wherein the packing fluid remains in place. These operations involving drilling, fracturing, and packing are well-working operations; and the oil base well-drilling fluids, well-fracturing

fluids, and well-packing fluids are all termed "oil base well-working fluids," as used in the following specification and claims.

U.S. Patent No. 3,041,275 discloses a composition suitable for use as a drilling fluid at high temperatures consisting essentially of from about 20 to about 70 parts by volume of a mineral oil, from about 80 to about 30 parts by volume of water, at least about two pounds per barrel of said composition of an amide of a gamma hydroxy carboxylic acid having from four to six carbon atoms and an aliphatic amine having an unsaturated hydrocarbon radical containing at least about 12 carbon atoms, at least about one pound per barrel of said composition of a soap selected from the group consisting of aluminum oleate and alkali metal soaps of organic acids containing from about 12 to about 20 carbon atoms, and said soap being in an oil-dispersible form, from 0 to about 600 pounds per barrel of said composition of a finely divided solid insoluble in said oil and said water, from 0 to about 20 pounds per barrel of said composition of a solid natural asphaltic mineral in finely divided form, and from 0 percent salt to a sufficient amount of salt to saturate the aqueous phase of said composition.

U.S. Patent No. 3,169,113 discloses an emusifier for a water-in-oil fracturing fluid, wherein said emulsifier contains one or both of (a) a nine to 18 carbon monocarboxylic acid fatty acid salt of a partial amide of a polyalkylene polyamine with two to six carbon alkylene groups and three to five amino nitrogens in which at least two amino groups are amidified with nine to 18 carbon monocarboxylic fatty acids and wherein there is at least one nonamidified amino group forming a salt with the acid and (b) a polyamide of an alkylene polyamine with two to six carbon alkylene groups and two to five amino nitrogens and a nine to 18 monocarboxylic fatty acid.

U.S. Patent No. 3,590,005 discloses emulsifier compositions comprising admixtures of (a) between about 10 percent and 90 percent by weight of an oxidized hydrocarbon wax-amine condesation product and (b) between about 90 percent and 10 percent of a metal salt of an oxidized hydrocarbon wax, said emulsifier compositions being particularly effective for preparing water-in-oil emulsions that are stable in the presence of electrolytes and at temperatures as high as about 260°C.

U.S. Patent No. 4,575,428 discloses a surfactant for use in invert emulsion drilling fluids, the invert emulsion drilling fluid produced therefrom, and a method of drilling, completing and working over a subterranean well utilizing said drilling fluid. The drilling fluid comprises an emulsion formed by producing a diamide having from between about 20 mole percent and about 35 mole percent of a polyamine, and from between about 30 mole percent and about 70 mole percent of a fatty acid having from between about six to about 20 carbon atoms therein, the diamide thereafter being further reacted with from between about 15 mole percent and about 35 mole percent of a tricarboxylic acid. The total amine value of said oligamide being from between about 10 to about 30, and the acid value of said oligamide being from between about 26 to about 46. When the surfactant is diluted to about 70 w/w percent concentration with a suitable solvent, the ES_3, as defined in the patent, of said emulsion drilling fluid will exceed about 400 volts, the ES_5 will be greater than the ES_4, and the ES_5 will be greater than about 1,000 volts. Alternatively, the electrical stability of the emulsion drilling fluid, when using the API Electrical Stability Test, should be at least about 1,000 volts.

U.S. Patent No. 4,658,036 discloses a process for the preparation of invert emulsifiers useful for oil-base drilling muds. The emulsifiers are prepared by reacting at least one tall oil fatty acid with acrylic acid, maleic anhydride, or fumaric acid. The product of this reaction is substantially reacted with diethylene triamine, and at least one tall oil fatty acid to give the invert emulsifier.

U.S. Patent No. 4,735,732 discloses a filtration control additive for use in invert emulsion drilling fluids; the method of preparing such additives; the invert emulsion drilling fluid produced therefrom; and a method of drilling, completing, and working over a subterranean well, utilizing such drilling fluid containing the filtration control additive which is utilized in a water-in-oil, emulsion-type subterranean drilling fluid. The additive comprises the pyrolyzed product obtained by intermixing and heating a finely divided humic acid-containing material and a primary amine having an alkyl radical of 10 to 20 carbon atoms or a primary amine having one alkyl-substituted phenyl radical, the alkyl radical having 10 to 20 carbon atoms. The amine may also be a secondary amine having at least one alkyl radical of eight to 20 carbon atoms.

U.S. Patent No. 4,876,017 discloses the use of a synthetic hydrocarbon compound, such as a polyalphalolefin, which may be combined with emulsifiers and thinners (functional additives) at a ratio of approximately 9:1, to serve as a downhole lubricant that is nontoxic and presents no destruction to marine life. In addition, the polyalphalolefin may be used at a higher ratio of the polyalphalolefin to functional additives to function as a spotting fluid for the removal of lodged tools downhole, exhibiting the same nontoxic qualities as when it is used as a lubricant.

U.S. Patent No. 5,045,219 discloses a composition and application thereof relating to a synthetic hydrocarbon compound, a polyalphaolefin liquid, blended in various concentrations with chemical oil and water emulsifiers, thinners and oil and water surface tension reducers, the concentration of polyalphaolefin liquid to that of the remaining portion of the blend being no less than 5 percent; blending the polyalphaolefin liquid and the emulsifiers in a blending tank containing water base drilling mud; circulating the blend of polyalphaolefin liquid and emulsifier with the water base drilling mud down hole, so that the blend of polyalphaolefin liquid emulsifier and water base drilling mud lubricates the drill string or reduces the differential pressure between the wall of the borehole and the drill string so that the drill string is free to rotate and drilling may be undertaken with less drag or torque. In another application, the polyalphaolefin blended with the emulsifier serves as a spotting fluid in order to unstick drill pipe that has become stuck.

U.S. Patent No. 6,211,139 discloses certain amine and quaternary ammonium compounds and formulations thereof that are said to be useful as, for instance, fabric softeners, paper debonders, hair conditioners, skin conditioners, paper deinking and ink flotation agents, asphalt emulsion agents, corrosion inhibitor agents, ore flotation agents, pesticide emulsion agents, car drying aid sprays, drilling fluid additives, and the like.

The disclosures of the foregoing are incorporated herein by reference in their entirety.

SUMMARY OF THE INVENTION

According to the present invention, fatty amines are reacted with polycarboxylic acids to form mixtures of mono-, di-, and tri-amides, which are excellent emulsifiers for oil-based drilling fluids, specially for synthetic oil-based fluids. Drilling fluids thus made have very high electrical stability (over 1,000 volts).

Oil-based drilling fluids that employ commercially available emulsifiers generally have low electrical stability and it is difficult to adjust the rheology thereof without affecting the electrical stability. The emulsifiers of the present invention make possible oil-based drilling fluids having extremely high electrical stabilities, which are indicative of invert emulsion stability.

The emulsifiers of the present invention are reaction products of fatty amines with polycarboxylic acids. The fatty amines can be primary amines, secondary amines, or tertiary amines. The polycarboxylic acid can be di- or tri-carboxylic acids. For example, primary tallow amine can be reacted with citric acid to form the emulsifier di-tallow citric amide. The emulsifier is then combined with a base oil to form the drilling fluid. The base oil can, for example, be a diesel, synthetic, or mineral oil. Preferably, the oil-based drilling-fluid is made of a polyalphaolefin (PAO) or paraffin as base oil and di-tallow citric amide as emulsifier, which provides a product having electrical stability of over 1,000 volts and adjustable rheology.

More particularly, the present invention is directed to a composition comprising a water-in-oil emulsion fluid for use in the drilling, completion or workover of a subterranean well, said emulsion fluid comprising:

A) a base comprising at least one liquid hydrocarbon;

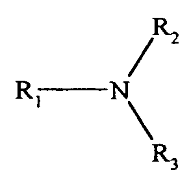
B) an aqueous phase; and

C) an emulsifier comprising at least one amide prepared by reacting at least one fatty amine with at least one polycarboxylic acid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A fatty amine is used in the process of the invention. The term "fatty amine," as employed herein, is an amine that contains one or more long-chain hydrocarbyl groups, which can be further substituted with other functional groups such as ether or hydroxyl groups.

The amines employed in the practice of the present invention are of the structural formula



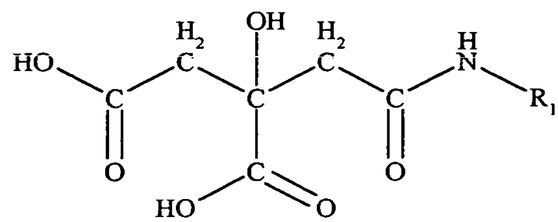
wherein R_1, R_2, and R_3 are selected from the group consisting of hydrogen, hydrocarbyl groups, and hydrocarbyl groups substituted with functional groups, provided that at least one of R_1, R_2, or R_3 is a C_8 or greater hydrocarbyl group, and is preferably a C_8 -C_{30} hydrocarbyl group. Suitable fatty amines include primary, secondary, tertiary, and ethoxylated or propoxylated amines. Examples include oleylamine, 1-dodecylamine, di-n-octadecylamine, tri(isodecyl)amine, dimethyl-n-decylamine, bis(2-hydroxyethyl)dodecylamine, tallow amine, bis(2-hydroxyethyl)tallowamine, and bis(2-hydroxypropyl)dodecylamine and the like.

While the amidification can be carried out with an appropriate quantity of one such amine, it is preferred for reasons of economy, product performance, and convenience to employ mixtures of amines, each corresponding to the structural formula R_1NH_2. For example, mixtures of fatty amines derived from various animal and vegetable origins are conveniently commercially available. One example of such material is tallow amines which, as is generally known in this field, is a mixture of fatty amines predominantly composed of fatty amines containing 14, 16, and 18 carbon atoms, and 0, 1, and 2 degrees of unsaturation. Other sources include coconut fatty amines and canola fatty amines, although any suitable fatty amine can be used. Amidification can be carried out under conventional conditions, well-known to the chemist in this field, allowing for the withdrawal of byproducts. The number of moles of fatty amine is selected to provide the desired average degree of amidification in the mixture of products formed upon amidification.

The polycarboxylic acids that can be reacted with the above-described amines to form the amides of the present invention include, for example, lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Pat. Nos. 821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane-cis, cis, cis-tetracarboxylic acid, cyclopentadienide pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid, phthalic acid and derivatives thereof, such as those disclosed in

British Pat. No. 1,425,343, and the like. Dicarboxylic and tricarboxylic acids are preferred, tricarboxylic acids more preferred, and citric acid most preferred.

Normally, in the amidification, at least one carboxylic acid function will remain unreacted with the amine. For example, particularly preferred amides for use in the practice of the present invention include those of the structures:



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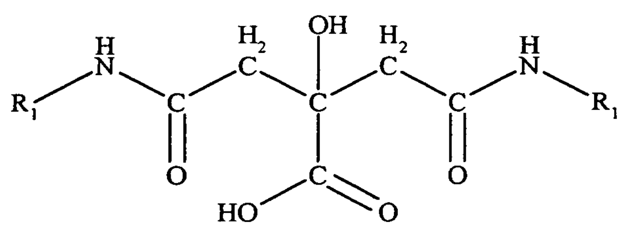

wherein R_1 is as described above.

The amine, e.g., tallow amine, can be reacted with the polycarboxylic acid, e.g., citric acid, to form the amides of the invention in the following ways.

Sample A

Preparation of a diamide from tallow amine and citric acid: a 500 mL flask was charged with Adogen-170 (150.0 gm), (Adogen 170 is tallow amine, a product made by Goldschmidt) followed by heating the flask to a temperature set at 100° C. After the temperature reaches 100° C, citric acid (55 gm) was carefully added so as to control the reaction temperature below 130° C. After completion of addition of citric acid, the reaction was continued at ca. 160° C for about another 1.5 hours so as to complete the reaction. The reaction was monitored by use of total amine value and acid value. IR, NMR, and GPC identified the structure of the prepared titled compound.

Sample B

Preparation of monoamide from tallow amine and citric acid: a 500 mL flask was charged with citric acid (57.64 gm) and MeOH (100 gm). The mixture was heated to 70° C and the citric acid was dissolved to form a solution. The mixture was stirred for 30 minutes at 70° C, and Adogen-170 (77.72 gm) was carefully added so as to control the reaction temperature below 80° C. A trap was set to collect the distillates. After completion of addition of Adogen 170, the reaction was continued at 90° C for another one hour and distillate (70 gm) was collected. The temperature was set at 135° C and the reaction was continued for another one hour, while a very small stream of N_2 gas was introduced. The reaction was monitored by use of total amine value and acid value. IR, NMR, and GPC identified the structure of the prepared titled compound.

Sample C

Preparation of triamide from tallow amine and citric acid: a 500 mL flask was charged with Adogen-170 (158.6 gm), followed by heating the flask to a temperature set set at 90° C. After the temperature reached 90° C, citric acid (38.6 gm) was carefully added so as to control the reaction temperature below 130° C. After completion of addition of citric acid, the reaction was continued at ca. 155-160° C for about another 2.5 hours so as to complete the reaction. The reaction was monitored by use of total amine value and acid value. IR, NMR, and GPC identified the structure of the prepared titled compound.

The equipment utilized in determining emulsion stability consists of a reliable circuit using a source of DC current in portable units (which provides a ramped, sinusoidal electrical signal) connected to a pair of parallel flat-plated electrodes. The voltage imposed across the electrodes can be increased rapidly until a predetermined amount of current flows. The measure of emulsion breakdown is indicated by current flow. Relative stability is indicated as a voltage at breakdown point. In the procedure utilizing such equipment, the electrodes are inserted into the drilling fluid sample to be tested. The voltage range multiplier that is applicable is selected. The voltage across the electrodes is increased until the instrument indicates emulsion breakdown. The voltage reading is recorded as an electrical stability number at a given temperature. Typically, this reading should be above about 1,000 volts for a laboratory-prepared emulsion mud. This test is referred to hereafter as the "API Electrical Stability Test."

Still another criterion for determining the preparation of a satisfactory emulsion for utilization in the present invention is a high temperature and high pressure filtration test and the emulsion stability of a prepared mud utilizing the surfactant of the present invention. On a

commercial and field basis, the filtration and emulsion stability tests of Sections 3 and 8, respectively, of the Recommended Practice Standard Procedure for Field Testing Oil-Based Drilling Fluids" (RP-138B, second edition, December 1, 1991), prepared by the American Petroleum Institute, can be easily utilized. The instrument utilized in the filtration test consists essentially of a controlled pressure source, a cell designed to withstand a working pressure of at least 1,000 PSI, a system for heating the cell, a suitable frame to hold the cell and heating system and a pressurized collection cell designed to withstand a working back pressure of at least 500 PSI to avoid flashing or evaporation of the filtrate at high temperatures.

Water-in-oil emulsions prepared in accordance with the present invention, utilizing the above described emulsifier compositions, comprise from about one to about 97 parts by weight of water or aqueous electrolyte solution as the dispersed phase, from about 99 to about three parts by weight of oleaginous material as the continuous phase, and at least about 1 percent and preferably between about 2 percent and 6 percent by weight, based on the weight of the aqueous and oleaginous phases of the emulsion, of the emulsifier composition of the present invention. It is particularly desirable that the emulsions contain from about 30 to about 70 parts by weight of water or aqueous electrolyte solution as the dispersed phase, from about 70 to about 30 parts by weight of oleaginous material as the continuous phase, and about 3 percent to 4 percent by weight, based on the weight of the aqueous and oleaginous phases of the emulsion, of the emulsifier composition of the present invention.

The emulsifier is evaluated in synthetic oil-based drilling fluid systems. The following is the preparation procedure of oil-based drilling fluids. Base fluid (either normal paraffin or polyalpha olefin) (173 mL) is measured into a 350 mL conical container. Fresh water (77 mL) is then added to the base fluid. A Hamilton-Beach mixer at medium speed is used as the

blending equipment. Two grams of organophilic clay is added while mixing. After ten minutes, two grams of lime, seven grams of organophilic lignite, and eight grams or a specified weight of emulsifier are mixed into the blend for five minutes. Barite (327 grams) is added next and mixing is carried out for another five minutes. Finally, 27 grams of calcium chloride is added and blended for ten minutes. The prepared oil-based mud is then evaluated for rheology properties and electrical stability.

The above mud is then aged in a roller oven. The roller oven temperature is set at 150° F (about 66° C). Mud is being sealed in aging cells. After the oven reaches the designed temperature, the cells are placed in the oven for 16 hours.

The shear stability is run with a Multi-mixer. At least three samples are tested at a time. Base oil (160 mL) is added to a 350 mL conical container, then emulsifier is added. The initial concentration of emulsifier will be near 1 to 2 grams. The lowest amount of emulsifier is where the mud water-wets within one hour shear time. A quantity of 43 grams of calcium chloride solution (33% by wt.) is further added to the container and mixing is carried out for five minutes. Three grams of organophilic clay is then added to the blend followed by 15 minutes of mixing. Four hundred grams of barite is added last, followed by 30 minutes of mixing. The sample temperature and electric stability are measured and recorded. This is followed by mixing for another 30 minutes, whereupon the sample temperature and electric stability are again measured and recorded.

In the practice of the present invention, the above described emulsifiers are combined with a base oil to form the drilling fluid. Any of the base oils known in the art can be used for this purpose, the most common being vegetable oil, mineral oil, and diesel oil.

Crude and refined oils were used as early as the 1920s to drill troublesome formations, free stuck pipe, and as completion and packer fluids. Later developments saw the use of No. 2 diesel oil as a common additive to mud systems. More recent environmental concerns over the toxicity of diesel oils required a base fluid change to less toxic refined mineral oils. Current industry requirements in offshore drilling are to have nontoxic fluids that can pass discharge guidelines as specified by the Environmental Protection Agency.

Overall, these types of oils suffer from many drawbacks, the most pertinent being that the oil is highly toxic to marine life. For example, should the oil in an offshore drilling operation spill over into the water, it has been determined that mineral oil or vegetable oil owing to its heavy oily nature will, in effect, coat the gills of marine animals and destroy valuable marine life. In fact, the Environmental Protection Agency has taken steps to assure that these types of oil are used under very stringent regulations during offshore drilling and, for the most part, in all likelihood should not be used at all. Vegetable oils have been used as substitutes offering a nontoxic alternative but have not proven to be effective performers in this application.

It is accordingly preferred in the practice of the present invention that a synthetic hydrocarbon, more particularly a polyalphalolefin, be employed. These synthetic hydrocarbons are highly effective in drilling fluid lubricants and spotting fluids and have a low order of toxicity.

Polyalphaolefin synthetic hydrocarbons are chemically pure, highly defined liquid polymers quite unlike the complex mixtures of hydrocarbons that comprise mineral oils. They are formed by the oligomerization of normal alpha olefins, which can be derived from ethylene. By altering the degree of oligomerization, the properties of the fluid can be modified. The

olefin oligomers are subsequently hydrogenated to lend stability to the molecule. Since the polyalphaolefin contains only carbon and hydrogen and conforms substantially to one kind of structure, the properties of the fluid are uniform and predictable. The preferred polyalphaolefins used in this invention range from a 2 centistoke to a 10 centistoke viscosity range.

The polyalphalolefins are especially useful in offshore applications or environmentally sensitive areas, since they are completely nontoxic to marine life, and therefore offer no threat in offshore application should a spill occur.

Organophilic clay, quaternary amine treated clay, is added to the water-in-oil mud to adjust mud rheology properties and, to some extent, filtration control. Organophilic lignite is also needed in the mud system to control filtration. Barite or other unhydratable, non-active solid is added to increase mud density.

Various features and aspects of the present invention are illustrated further in the examples that follow. While these examples are presented to show one skilled in the art how to operate within the scope of the invention, they are not intended in any way to serve as a limitation upon the scope of the invention.

Examples

The following tables show the test data that were obtained following the Standard Procedure for Field Testing Oil-based Drilling Fluids. (API Recommended Practice 13B-2). Fan 35A, HTHP filtration test cell, and electric stability tester are the apparatus involved to acquire these data. Aging is done in a roller oven at 150° F for 16 hours.

Two synthetic base oils were evaluated. One is normal paraffin, the other is a polyalpha olefin. The prepared mud is a14 lb/gal, 70/30 oil/water ratio, 25% calcium chloride water-phase salinity oil mud. Experimental emulsifiers A, B, and C were synthesized and compared with Witcomul 3241. Emulsifier Samples A, B, and C were made by the above-described methods.

Witcomul 3241 (Crompton Corporation) is a widely used, commercially available emulsifier product in the market. It is used as a benchmark. In the following tables, the normal paraffin was a mixture of C_{13} to C_{15} chain length paraffin, the polyalpha olefin was an isomerized C_{16}/C_{18} alpha olefins, the organophilic lignite was Duraton HT, and the organophilic clay was Gelton HT.

Mud Test – Normal Paraffin

Base oil normal paraffin, mL	173	173	173	173	173
Fresh water, mL	77	77	77	77	77
Organophilic clay, grams	2	2	2	2	2
Emulsifier, Sample A, grams	8	6	5	4	3
Lime, grams	2	2	2	2	2
Organophilic lignite, grams	7	7	7	7	7
Barite, grams	327	327	327	327	327
Calcium chloride, grams	27	27	27	27	27

Test temperature, °F	120	120	120	120	120
600 rpm	71	80	79	75	70
300 rpm	44	52	50	50	46
200 rpm	33	41	40	40	37
100 rpm	22	28	29	29	27
5 rpm	8	9	10	12	13
3 rpm	6	7	9	10	11

Electrical stability, V	1037	740	791	834	877
Plastic viscosity, cp	27	28	29	25	24
Yield point, lb/100 sq. feet	17	24	21	25	22
10 sec/10 min. gel, lb/100 sq. feet	7/8	8/10	10/12	10/15	11/19

After rolling 16 hours at 150° F					
Test temperature, ° F	120	120	120	120	120
600 rpm	62	96	79	68	69
300 rpm	37	60	50	43	41
200 rpm	28	46	39	33	31
100 rpm	17	30	26	22	21
6 rpm	5	9	9	9	9
3 rpm	4	7	8	8	8

Electrical stability, V	1155	1476	1267	1030	715
Plastic viscosity, cp	25	36	29	25	28
Yield point, lb/100 sq. feet	12	24	21	18	13
10 sec/10 min gel, lb/100 sq. feet	5/10	9/12	10/13	10/13	9/13

HTHP filtrate temperature, 300° F					
filtrate, total volume, mL	1.2	1.5	2	2.1	2.2
filtrate, oil volume, mL	1.2	1.5	2	2.1	2.2
filtrate, water volume, mL	0	0	0	0	0
filtrate, emulsion volume, mL	0	0	0	0	0

Shear Stability test – Polyalpha Olefin

Base oil	PAO	PAO	Paraffin	Paraffin
Volume, mL	160	160	160	160
Emulsifier, Witcomul 3241, grams	2		2	
Emulsifier, Emulsifier B, grams		2		2
Calcium chloride, 33% solution	43	43	43	43
Organophilic clay, grams	3	3	3	3
Barite, grams	327	327	327	327
Measure sample temperature, °F	119	120	102	99
Measure sample ES, V	774	626	1103	724
Measure sample temperature, °F	129	117	119	115
Measure sample ES, V	868	840	1270	885

Shear Stability – Normal Paraffin

Base oil normal paraffin, mL	160	160	160	160
Emulsifier, Witcomul 3241, grams	2			
Emulsifier, Emulsifier A, grams		3		
Emulsifier, oxidized tall oil, g		0.5		
Emulsifier, Emulsifier B, grams			2	
Emulsifier, Emulsifier C, grams				2
Calcium chloride, 33% solution	43	43	43	43
Organophilic clay, grams	3	3	3	3
Barite, grams	400	400	400	400
Measure sample temperature, °F	111	115	99	97
Measure sample ES, V	1103	700	616	415
Measure sample temperature, °F	119	120	106	103
Measure sample ES, V	1270	750	960	600

The emulsifier usage is the minimum amount that can pass the shear stability test.

Mud test – Polyalpha Olefin (PAO)

Base oil PAO, mL	173	173	173	173	173
Fresh water, mL	77	77	77	77	77
Organophilic clay, grams	2	2	2	2	2
Emulsifier, Sample A, grams	8	6	5	4	3
Lime, grams	2	2	2	2	2
Organophilic lignite, grams	7	7	7	7	7
Barite, grams	327	327	327	327	327
Calcium chloride, grams	27	27	27	27	27

Test temperature, °F	120	120	120	120	120
600 rpm	120	154	134	132	125
300 rpm	82	112	97	97	92
200 rpm	67	94	81	82	78
100 rpm	50	70	62	63	60
5 rpm	20	32	29	30	30
3 rpm	17	28	26	28	29

Electrical stability, V	1869	1074	1045	872	726
Plastic viscosity, cp	38	42	37	35	33
Yield point, lb/100 sq. feet	44	70	60	62	59
10 sec/10 min. gel, lb/100 sq. feet	17/22	26/32	25/34	27/34	28/36

After rolling 16 hours at 150° F					
Test temperature, °F	120	120	120	120	120
600 rpm	111	147	115	107	100
300 rpm	75	103	77	71	67
200 rpm	61	85	64	58	53
100 rpm	44	63	47	42	40
6 rpm	20	30	24	20	20
3 rpm	18	28	22	19	18

Electrical stability, V	1769	1710	1457	1158	811
Plastic viscosity, cp	36	44	38	36	33
Yield point, lb/100 sq feet	39	59	39	35	34
10 sec/10 min. gel, lb/100 sq feet	22/28	32/40	25/30	23/29	21/28

HTHP filtrate temperature, 300° F					
filtrate, total volume, mL	1	1.5	2	2	2.4
filtrate, oil volume, mL	1	1.5	2	2	2.4
filtrate, water volume, mL	0	0	0	0	0
filtrate, emulsion volume, mL	0	0	0	0	0

As shown in the above tables, the oil-based drilling fluids mase with current emulsifiers have an extremely high stability and low HTHP (high temperature high pressure) filtration.

In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection to be afforded the invention.